

Charge Transfer in Cluster–Atom Collisions Studied with Non-Adiabatic Quantum Molecular Dynamics

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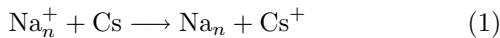
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Charge transfer in collisions of Na_n^+ cluster ions with Cs atoms is investigated theoretically in the microscopic framework of non-adiabatic quantum molecular dynamics. The competing reaction channels and related processes affecting the charge transfer (electronic excitations, fragmentation, temperature) are described. Absolute charge transfer cross sections for $\text{Na}_n^+(2.7 \text{ keV}) + \text{Cs} \longrightarrow \text{Na}_n + \text{Cs}^+$ have been calculated in the size range $4 \leq n \leq 11$ reproducing the size dependence of the experimental cross sections. The energy dependence of the cross section is predicted for $n = 4, 7, 9$. An exotic charge transfer channel producing Cs^- is found to have a finite probability.

34.70.+e, 36.40.Qv, 31.15.Qg

Charge transfer represents one of the fundamental atomic interactions. In the last decades, large progress has been made in the understanding of charge transfer mainly for two borderline cases: the elementary ion–atom reaction [1] and the complex ion–surface interaction [2]. In the recent past, however, there has been a flurry of activity to close the gap between the two fields by investigating the intermediate case of ion–cluster collisions [3–18]. In general, the basic aspect of cluster collisions consists in the simultaneous occurrence and mutual coupling of electronic transitions (charge transfer, excitation, ionization) and nuclear-core excitations (vibration, rotation, fragmentation) in a system, where the number of electronic and nuclear degrees of freedom is *large but finite*. In particular, collision induced dissociation (CID) will compete with charge transfer (CT) in such collisions.

Already, in one of the first experiments with mass-selected cluster beams, CT and CID were investigated for $\text{Na}_n^+ + \text{Cs}$ [3,4] and $\text{K}_n^+ + \text{Cs}$ [4] collisions. An important result of these novel experiments was the direct determination of the CT cross section for the neutralization of the parent cluster ion, i.e.



by measuring the neutral products associated with the process (1) but discriminating neutral products originating from CID. Further experimental studies of CT in collisions of cluster cations with atoms [5–10], molecules [7]

and clusters [11,9] have been performed providing a considerable amount of data. Multiple CT processes accompanied by fragmentation have been observed in collisions of highly charged ions with fullerenes [12,13] and sodium clusters [14].

This enormous experimental progress was accompanied by the development of a number of theoretical descriptions of CT reactions in cluster collisions. In Ref. [4], a two-state model of (near) resonant CT was presented. Classical barrier models [15,16] have been applied to distant collisions of C_{60} with highly charged ions. Semi-microscopic descriptions of CT, which are based on the jellium approximation [17] or on phenomenological single-particle potentials [18], have also been suggested. However, the combined description of CT *and* fragmentation or, more generally, a simultaneous treatment of electronic *and* nuclear degrees of freedom in non-adiabatic cluster collisions is still an unsolved problem.

Recently, a universal microscopic approach called non-adiabatic quantum molecular dynamics (NA-QMD) has been developed, which describes classical atomic motion simultaneously and self-consistently with electronic transitions in atomic many-body systems [19]. In this paper, we present a fully microscopic analysis of CT and fragmentation in cluster collisions applying the NA-QMD theory to $\text{Na}_n^+ + \text{Cs}$.

The NA-QMD approach has been derived [19] on the basis of the time-dependent density functional theory [20], whereby the Kohn–Sham formalism within the time-dependent local density approximation is used. Resulting from an LCAO ansatz for the Kohn–Sham orbitals a set of coupled differential equations for the time-dependent coefficients is obtained to determine the time evolution of the electronic density as the consequence of the classical atomic motion. Simultaneously, Newton’s equations of motion with explicitly time-dependent forces have to be solved reflecting the possible energy transfer between the classical system of ionic cores and the quantum-mechanical system of valence electrons. Details of the procedure to calculate expectation values of observables or probabilities for specific electronic transitions (defined by the time-dependent electronic density) as well as of the different fragmentation channels (obtained from classical

trajectories) will be given elsewhere [21].

To elucidate the different physical processes determining the absolute cross section of the CT reaction (1), we have performed a detailed study of the system $\text{Na}_4^+ + \text{Cs}$ at a lab collision energy of $E_{\text{lab}} = 2.7 \text{ keV}$. The cluster projectile is prepared initially in its electronic and geometric ground state (rhombic, D_{2h}). In Fig. 1, the time evolution of the calculated mean charge located at the Cs atom $\langle q_{\text{Cs}} \rangle(t)$ (obtained from a population analysis) as well as of the kinetic-energy difference $\Delta E_{\text{kin}}(t) = E_{\text{c.m.}} - E_{\text{kin}}(t)$, where $E_{\text{c.m.}}$ and $E_{\text{kin}}(t)$ are the collision energy and the total kinetic energy, respectively, both referred to the center-of-mass frame, are presented for two collision events with the same impact parameter ($b = 9 \text{ a.u.}$) but different initial orientations of the cluster with respect to the beam axis (see inserts (a) and (b) in Fig. 1). The quantity $\langle q_{\text{Cs}} \rangle(t)$ characterizes the quantum dynamics of CT, whereas $\Delta E_{\text{kin}}(t)$ describes the energy flow in the classical (ionic) degrees of freedom. A strong dependence of both quantities on the initial orientation of the cluster is observed. In the example (a), nearly compensating charge fluctuations during the interaction lead finally to $\langle q_{\text{Cs}} \rangle \approx 0$, and the event corresponds to a nearly elastic scattering $\Delta E_{\text{kin}} \approx 0$. In contrast, the large CT in the case (b) $\langle q_{\text{Cs}} \rangle \approx 0.75$ is accompanied by a considerable energy loss of $\Delta E_{\text{kin}} \approx 0.34 \text{ eV}$. An endothermic character is typical for most collision events with appreciable CT, even at larger impact parameters, where no vibrational excitation of the cluster occurs. Comparing the ionization potentials of the Cs atom (3.89 eV) and the Na_4 cluster (4.24 eV [22]) and assuming a CT that results in the electronic ground state of Na_4 , one should expect an exothermic reaction with $\Delta E_{\text{kin}} \approx -0.35 \text{ eV}$. That this is not the case indicates that the CT process produces an electronically excited Na_4 cluster.

The calculation of CT cross sections requires a detailed analysis of the final electronic and atomic states and, in particular, the careful consideration of CT probabilities for different reaction channels. To start with a transparent classification, we define integral CT probabilities, which are the probabilities $P(\text{Cs}^q)$ to find the Cs atom in the charge state q in the exit channel, where q is an integer and $\sum_q P(\text{Cs}^q) = 1$. These probabilities describe the primary CT ($q \neq 0$) and scattering ($q = 0$) processes without regard to the further evolution of the cluster, i.e. to the possible fragmentation. The related CT cross sections can be directly measured by detecting the formed Cs ions. The probabilities $P(\text{Cs}^q)$, calculated as an average of the results obtained with about 300 different initial orientations of the cluster per impact parameter b , are shown as a function of b in the upper panel of Fig. 2. The CT leading to Cs^+ ions and the scattering without CT have nearly equal probabilities $P(\text{Cs}^+)$ and $P(\text{Cs})$, respectively, for impact parameters $b \leq 8 \text{ a.u.}$. As the graph of $P(\text{Cs}^+)$ indicates, CT takes

place with remarkable probability up to impact parameters of $b \approx 15 \text{ a.u.}$, which is more than twice the long half-axis ($R = 5.7 \text{ a.u.}$) of the Na_4 rhombus. Surprisingly, the calculations also yield a finite probability $P(\text{Cs}^-)$ for an electron transfer to the Cs atom, which represents an interesting prediction for future experimental studies.

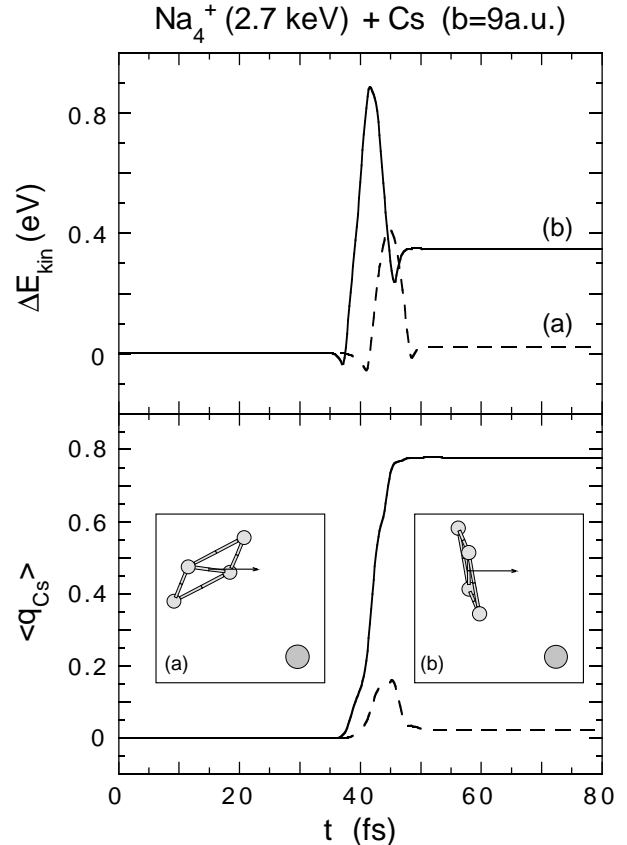


FIG. 1. Calculated kinetic-energy difference ΔE_{kin} (upper panel) and mean value of the charge located at the Cs atom $\langle q_{\text{Cs}} \rangle$ (lower panel) as functions of time t for the two initial collision geometries illustrated in the inserts (a) and (b). The dashed and solid lines correspond to the cases (a) and (b), respectively.

The b -weighted integration of $P(\text{Cs}^+)$ leads to a total CT cross section of $\sigma(\text{Cs}^+) = (38.2 \pm 2.1) \text{ \AA}^2$. For comparison, the “geometrical” cross section of the cluster is about $\sigma_0 \approx \pi R^2 \approx 29 \text{ \AA}^2$ and the measured value is $\sigma^{\text{exp}}(\text{Na}_4) = (17 \pm 3) \text{ \AA}^2$ [3]. It is important to realize, however, that, instead of Cs^+ , the signal of the neutralized Na_4 was detected in the measurements [3]. The “survival” probability of the Na_4 cluster after the primary CT is given by $P(\text{Cs}^+) \cdot [1 - P_{\text{Fr}}]$, where P_{Fr} is the total fragmentation probability. In cluster collisions, fragmentation can be induced through three mechanisms characterized by different time scales [21,23,24]. These are large momentum transfer between atoms of the projectile and of the target, electronic excitation followed

by energy transfer via electron-vibrational coupling, and statistical fragmentation. Whereas the first two mechanisms are precisely described by the NA-QMD theory and automatically accounted for in the actual calculations (this has been shown in comparisons with experimental data on CID [24]), the total probabilities of the different fragmentation channels can be determined from the calculated internal (vibrational and electronic) excitation energy of the cluster using statistical arguments [21]. The calculated total fragmentation probability P_{Fr} and the probability $P(\text{Na}_4)$ to have a neutral Na_4 cluster in the exit channel are shown as a function of b in the lower panel of Fig. 2.

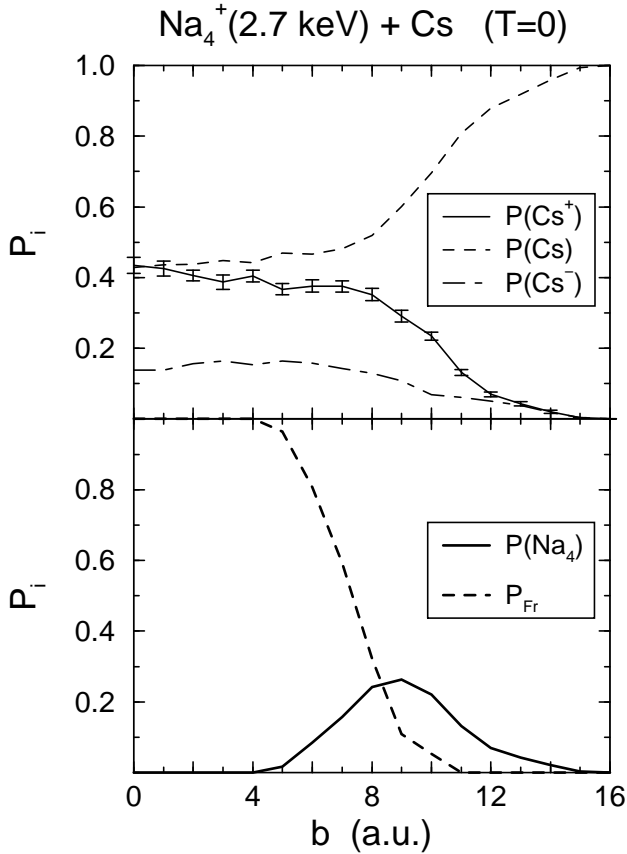


FIG. 2. Calculated integral CT probabilities $P(\text{Cs}^+)$, $P(\text{Cs})$, $P(\text{Cs}^-)$ [upper panel], and fragmentation P_{Fr} and CT probabilities $P(\text{Na}_4)$ [lower panel] as functions of the impact parameter b for Na_4^+ chosen initially at $T = 0 \text{ K}$ in its lowest-energy structure (see text). The length of the error bars is given by $2s_D$, where s_D is the standard deviation of the orientation average.

Fragmentation occurs with high and then decreasing probability up to $b \approx 11 \text{ a.u.}$, and the computed total fragmentation cross section of $\sigma_{\text{Fr}} = 49.4 \text{ \AA}^2$ exceeds the geometrical cross section considerably. The CT probability $P(\text{Na}_4)$ peaks around $b \approx 9 \text{ a.u.}$, which is larger than the cluster “radius” R . The CT cross section

$\sigma(\text{Na}_4) = 20.2 \text{ \AA}^2$ is still slightly larger than the experimental value.

The calculations presented so far have been carried out with zero initial temperature of the cluster, whereas under the experimental conditions [3,4] “liquid” cluster ions are used resulting from the laser ionization to produce the cluster beam [25]. To take into account the temperature effect, we have repeated the procedure described above with excited clusters in the initial state, where the total excitation energy was chosen to be slightly below the dissociation energies of the neutral as well as of the cationic cluster. The initial configurations of the excited clusters for the simulation of the collisions were produced in equilibration runs of 300 ps in length. The calculated CT cross section $\sigma(\text{Na}_4) = 16.8 \text{ \AA}^2$ obtained with “liquid” cluster ions is in perfect agreement with the experimental result.

The theoretical and experimental [3] CT cross sections are compared as a function of the cluster size n in Fig. 3. The theoretical results were obtained with “liquid” cluster ions in the initial state. Except for the case of $n = 5$, the agreement of the computed and measured data can be qualified as perfect, since these data are *absolute* cross sections. The statistical uncertainties of the calculated cross sections reflect the strong dependence of the outcome of the collision process on the initial configuration. These uncertainties could be reduced further only at a very high computational cost [21]. The overestimated cross section in the case $n = 5$ results from contributions of a particular isomer, for which accidentally a (quasi-) resonant CT with Cs occurs [21].

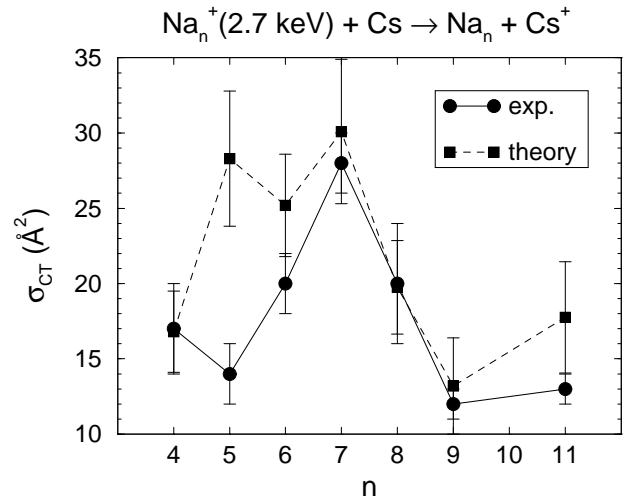


FIG. 3. Calculated and measured [3] CT cross sections $\sigma_{\text{CT}}(\text{Na}_n)$. The theoretical error bars result from the statistical uncertainty $2s_D$ (cf. Fig. 2).

The distinct maximum of the experimental CT cross section at $n = 7$ is reproduced by the calculations. This maximum, however, may be peculiar to the particular

collision energy. In the experimental investigation of $K_n^+ + Cs$ collisions [4] a very strong dependence of the CT cross section on the collision energy has been found (cf. Fig. 4 in Ref. [4]). In order to examine this aspect and to stimulate further experimental investigations, we have calculated the CT cross section over a wide range of the (center-of-mass) collision energy (0.1 ... 30 keV) for $n = 4, 7, 9$. The results are shown in Fig. 4. The absolute CT cross section for $n = 7$ exceeds those for $n = 4$ and $n = 9$ over the entire energy range considered. Consequently, the large CT cross section in $Na_7^+ + Cs$ collisions should be attributed to the specific electronic structure of Na_7^+ providing favorable, i.e. near resonant conditions for CT in collisions with Cs.

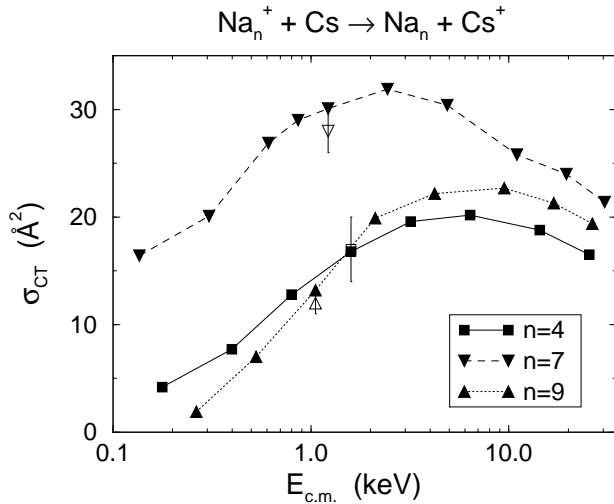


FIG. 4. Calculated collision energy dependence of the CT cross section $\sigma_{CT}(Na_n)$ for $n = 4, 7, 9$ (full symbols). The experimental data (open symbols with error bars; [3]) correspond to the same lab collision energy of $E_{lab} = 2.7$ keV.

In summary, we have presented results of a fully microscopic analysis of CT and fragmentation in cluster-ion – atom collisions based on NA-QMD simulations. The detailed study of $Na_4^+(2.7 \text{ keV}) + Cs$ collisions revealed the role of the different physical processes associated with CT in cluster collisions (electronic excitations, fragmentation, temperature effects). An exotic “inverse” CT process leading to Cs^- is predicted. The calculated absolute CT cross sections for $Na_n^+(2.7 \text{ keV}) + Cs$ ($4 \leq n \leq 11$) are in good agreement with the experimental data. The energy dependence of the CT cross section is predicted for several cluster sizes ($n = 4, 7, 9$) in order to encourage further experimental studies.

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